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TRITERPENOID SAPONINS FROM LEAVES OF *PITTOSPORUM UNDULATUM*

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Key Word Index—*Pittosporum undulatum*; Pittosporaceae; triterpenoid saponin; deacylsaponin; A_1-barrigenol 3-*O*-glycoside.

Abstract—Two triterpenoid saponins obtained from the leaves of *Pittosporum undulatum* were characterized on the basis of chemical and spectral evidence as a mixture of 22-*O*-(2-methylbutyloyl)- and 22-*O*-(3,3-dimethylacryloyl)-A_1-barrigenol 3-*O*-β-D-glucopyranosyl-(1 → 2)-[β-D-galactopyranosyl-(1 → 3)]-β-D-glucopyranosiduronic acid and 3-*O*-β-D-glucopyranosyl-(1 → 2)-{α-L-arabinopyranosyl-(1 → 3)-[α-L-arabinofuranosyl-(1 → 4)]}-β-D-glucopyranosiduronic acid. The sugar moieties are the novel oligosaccharides found in A_1-barrigenol glycosides.

INTRODUCTION

As described in the preceding paper [1], three acylated triterpenoids were obtained on acid hydrolysis of a fraction of the methanol extract of the leaves of *Pittosporum undulatum*, and identified as 22-*O*-(2-methylbutyloyl)- and 22-*O*-(3,3-dimethylacryloyl)-A_1-barrigenol (**1** and **2**), and 16-*O*-acetyl-camelliagenin A.

In the continuation of our study the various parent glycosides in the leaves were surveyed. This paper deals with the isolation and characterization of two triterpenoid saponins, PS-A (**3**) and PS-B (**4**).

RESULTS AND DISCUSSION

A glycoside mixture obtained from the methanol extract of the leaves was fractionated by normal- and reverse-phase column chromatography to give two compounds named PS-A (**3**) and PS-B (**4**). Compound **3**, as well as **4**, showed a single spot on normal- and reverse-phase TLC and one peak on reverse-phase HPLC. However, they afforded two acylated aglycones, **1** and **2**, on hydrolysis with a crude hesperidinase. Thus, **3** and **4** were regarded as mixtures of the glycosides of **1** and **2**, respectively.

On treatment with alkali, **3** gave a deacyl compound (**5**), which was hydrolysed with acid to yield A_1-barrigenol (**6**), glucose (glc), galactose (gal) and glucuronic acid (glr). Methylation of **5** with CH_2N_2 provided monomethyl ester (**7**), which showed in the ^{13}C NMR spectrum three anomeric carbon signals. The permethylate (**8**) of **5** obtained by the Hakomori method [2] exhibited the molecular ion peak at m/z 1186 in a field desorption mass spectrum (FDMS). These data indicate **5** to consist of 1 mol each of **6**, glc, gal and glr.

Methanolysis of **8** yielded an aglycone (**9**) and three different methylated monosaccharides. An acetate (**10**) of **9** showed in the ^1H NMR spectrum the signals of one acetoxy and four methoxy groups, together with a triplet-like signal at δ4.49 ascribable to the proton at C-3 bearing the acetoxy group [3]. Therefore **9** and **10** were regarded as the 15,16,22,28-tetra-*O*-methyl ether of **6** and its 3-*O*-acetate, respectively. Two of the three methylated monosaccharides were identified as methyl pyranosides of 2,3,4,6-tetra-*O*-methyl-glucose (S-1) and -galactose (S-2). Therefore, compound **5** was considered to have a branched trisaccharide, glucosyl-[galactosyl]-glucuronic acid, combined with the 3-hydroxy group of **6**.

Reduction of **8** with $NaBH_4$ followed by methylation of the product afforded a compound (**11**) which was methanolysed to give **9**, S-1, S-2 and the methyl pyranoside of 4,6-di-*O*-methyl-glucose. Thus, the glc and gal units in the sugar moiety of **5** are combined with the 2- and 3-, or 3- and 2-hydroxy groups of glr, respectively.

When **11** was treated with dilute HCl in MeOH, three products were provided. The major one was isolated and methylated to give a compound (**12**), which gave, on methanolysis, compound **9**, S-1 and methyl 3,4,6-tri-*O*-methyl-glucopyranoside. This indicated **12** to be the permethylate of glucosyl-(1 → 2)-glucoside of **6** and hence, if glc, gal and glr are assumed to be the most commonly found D-series, the oligosaccharide moiety of **5** is D-glucopyranosyl-(1 → 2)-[D-galactopyranosyl-(1 → 3)]-D-glucopyranosyluronic acid. The ^1H NMR spectrum of **8** showed three anomeric proton signals of sugar units as doublets with large J values (6, 8 and 8 Hz) indicating their β-linkage [3].

Consequently, compound **5** is A_1-barrigenol 3-*O*-β-D-glucopyranosyl-(1 → 2)-[β-D-galactopyranosyl-(1 → 3)]-β-D-glucopyranosiduronic acid.

Compound **4** was hydrolysed with alkali to give **13**. On the basis of the result of acid hydrolysis of **13** and the ^{13}C NMR and FDMS spectra of its monomethyl ester (**14**) and permethylate (**15**), compound **13** was regarded to be composed of 1 mol each of **6**, glr and D-glucose and two moles of L-arabinose.

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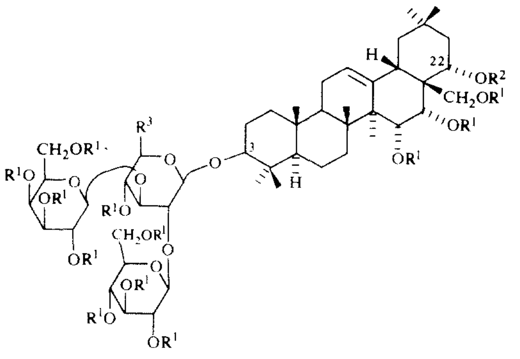
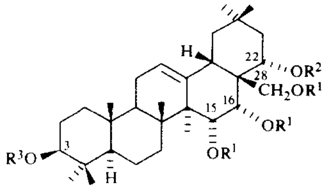
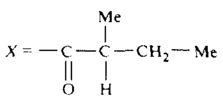
‡To whom correspondence should be addressed.

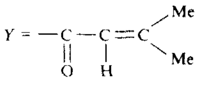


	R¹	R²	R³
3	H	*X* or *Y*	COOH
21	H	*X* or *Y*	COOMe
5	H	H	COOH
7	H	H	COOMe
8	Me	Me	COOMe
11	Me	Me	CH₂OMe

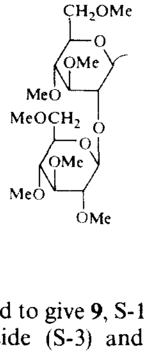




$X = -\mathrm{C}(=\mathrm{O})-\mathrm{CH}(\mathrm{Me})-\mathrm{CH_2}-\mathrm{Me}$



$Y = -\mathrm{C}(=\mathrm{O})-\mathrm{CH}{=}\mathrm{C}(\mathrm{Me})_2$

	R¹	R²	R³
1	H	*X*	H
2	H	*Y*	H
6	H	H	H
9	Me	Me	H
10	Me	Me	Ac
12	Me	Me	

Compound **15** was methanolysed to give **9**, S-1, methyl 2,3,4-tri-*O*-methyl-arabinopyranoside (S-3) and methyl 2,3,5-tri-*O*-methyl-arabinofuranoside (S-4). When **15** was subjected to reduction with $NaBH_4$, followed by methylation with the Hakomori method, a product (**16**) was obtained which was cleaved on methanolysis to yield **9**, S-1, S-3, S-4 and methyl 6-*O*-methyl-glucopyranoside. The above results show that **13** is the 3-*O*-glycoside of **6** and that glucopyranose, arabinopyranose and arabinofuranose are joined with the 2-, 3- and 4-hydroxy groups of glucopyranosyluronic acid. The structure of the sugar moiety of **13** was determined as follows.

Hydrolysis of **13** with a crude hesperidinase afforded a prosapogenin (**17**). Examination of the acid hydrolysis products of **17** and the FDMS and ^{1}H NMR spectral data of the permethylate (**18**) of the reduction product of **17** indicated that **17** was a triglycoside possessing 1 mol each of glucopyranosyluronic acid, arabinopyranose and arabinofuranose. Methylated monosaccharides obtained by methanolysis of **18** were identified as S-3, S-4 and the methyl pyranoside of 2,6-di-*O*-methyl-glucose. Therefore, the site of linkage of glc in the sugar moiety of **13** should be the 2-hydroxy of glr. On the other hand, acid hydrolysis of **13** under mild conditions gave a prosapogenin (**19**) which was different from **17**. The chemical and spectral data of **19** and the permethylate (**20**) of its reduction product indicated that **19** was a triglycoside where arabinofuranose in **13** was removed. Methanolysis of **20** afforded S-1, S-3 and methyl 4,6-di-*O*-methyl-glucopyranoside. Therefore, if glr is presumed to be the D-series, compound **19** is the D-glucopyranosyl-(1 → 2)-[L-arabinopyranosyl-(1 → 3)]-D-glucopyranosiduronic acid of **6**, and **13** is the D-glucopyranosyl-(1 → 2)-{L-arabinopyranosyl-(1 → 3)-[L-arabinofuranosyl-(1 → 4)]}-D-glucopyranosiduronic acid of **6**.

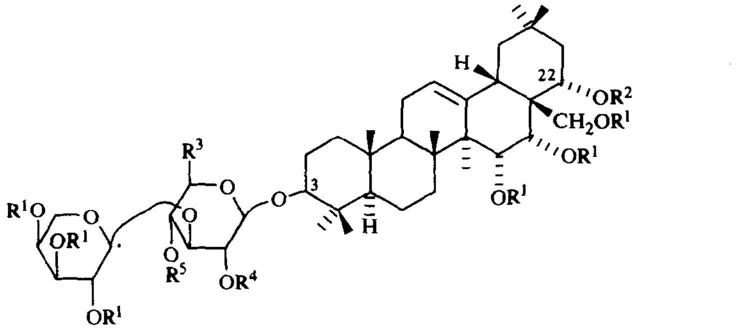
The configurations of the D-glucopyranosyl, D-glucopyranosyluronic acid and L-arabinopyranosyl units were regarded, respectively, to be β, β and α by their anomeric proton signals (each a doublet, $J = 8$, 6 and 6 Hz) [3, 4] in the ^{1}H NMR spectrum of **15**. The arabinofuranose unit was considered to have the α-configuration by comparison of its anomeric proton signal (δ 5.08, *s*) in the ^{1}H NMR spectrum of **15** with those of the methyl furanosides of 2,3,5-tri-*O*-methyl-α- and β-L-arabinose [5]. Therefore, it follows that **13** is A_1-barrigenol 3-*O*-β-D-glucopyranosyl-(1 → 2)-{α-L-arabinopyranosyl-(1 → 3)-[α-L-arabinofuranosyl-(1 → 4)]}-β-D-glucopyranosiduronic acid.

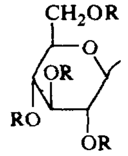
Methylation of **3** and **4** with CH_2N_2 afforded, respectively, monomethyl esters **21** and **22** and their ^{13}C NMR spectra showed three (in **21**) and four (in **22**) anomeric carbon signals and three ester carbonyl carbon signals (δ 176.2, 166.6 and 170.0 in **21**; 176.3, 166.6 and 170.3 in **22**). Accordingly, **3** and **4** are assumed to be mixtures of the 22-*O*-2-methylbutylate and 3,3-dimethylacrylates of **5** and **13**, respectively.

There has been a report on an A_1-barrigenol glycoside (deacyl boninsaponin A) which was obtained from *Schima mertensiana* [6]. Deacsaponins **5** and **13** are, to the authors' knowledge, new A_1-barrigenol glycosides.

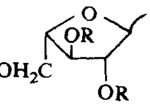
EXPERIMENTAL

For general methods, except for those described below, refer to the preceding paper [1]. Conditions of GC (FID mode): (a) glass column (1.2 m × 4 mm) packed with 5 % 1,4-butanediol succinate on shimalite W (60–80 mesh), column temp. 140°; (b) glass column (1.2 m × 4 mm) packed with 1 % neopentyl glycol succinate polyester on chromosorb W (AW)-DMCS (60–80 mesh), column temp. 145°. Solvent systems of TLC [silica gel, Rp-18 (reverse phase) and Avicel]: (a) $CHCl_3$–MeOH–HOAc–H_2O (15:9:1:2), (b) C_6H_6–Me_2CO (2:1), (c) 75 % MeOH,





R = H, Glc
R = Me, Glc(Me)



R = H, Ara
R = Me, Ara(Me)

	R¹	R²	R³	R⁴	R⁵
4	H	*X* or *Y*	COOH	Glc	Ara
22	H	*X* or *Y*	COOMe	Glc	Ara
13	H	H	COOH	Glc	Ara
14	H	H	COOMe	Glc	Ara
15	Me	Me	COOMe	Glc(Me)	Ara(Me)
16	Me	Me	CH_2OMe	Glc(Me)	Ara(Me)
17	H	H	COOH	H	Ara
18	Me	Me	CH_2OMe	Me	Ara(Me)
19	H	H	COOH	Glc	H
20	Me	Me	CH_2OMe	Glc(Me)	Me

(d) upper layer of *n*-BuOH–pyridine–H_2O (6:2:3)+pyridine, (e) upper layer of *n*-BuOH–HOAc–H_2O (4:1:5). FDMS were taken at +2.6–3.5 kV for the field anode and −5 kV for the slotted cathode plate, an ion source pressure of *ca* 10^{-7} Torr and emitter heating current of 17–21 mA.

Isolation. A saponin mixture (16 g), obtained from the fresh leaves, showing two major spots (R_f 0.54, 0.47) on TLC (silica gel; solvent a) was chromatographed on silica gel (eluant $CHCl_3$–MeOH–HOAc–H_2O, 4:1:1:0.2) to give two fractions, fractions 1 (R_f 0.54) and 2 (R_f 0.47). Each fraction was passed through a Sephadex LH-20 column (eluant MeOH). Fraction 1 showed seven spots on TLC (RP-18; solvent c) and was separated by reverse-phase (RP-18) CC (eluant 65% MeOH) to give the major component PS-A (**3**, 0.72 g, R_f 0.42). Fraction 2 showed five spots on TLC (RP-18; solvent c) and the major component, PS-B (**4**, 0.78 g, R_f 0.50) was obtained in the same manner as in **3**.

PS-A (**3**). Colourless needles (from MeOH), mp 273–278° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3370 (OH), 1700, 1690 (ester), 1610 (COO^-). Homogeneous on TLC (silica gel; solvent a and RP-18; solvent c) and on HPLC (column, Radial-Pak A; solvent 70% MeOH). Compound **3** was hydrolysed with a crude hesperidinase to give 22-*O*-(2-methylbutyloyl)- and 22-*O*-(3,3-dimethylacryloyl)-A_1-barrigenol (**1** and **2**) (see the preceding paper [1]). Methylation of **3** with CH_2N_2 in MeOH afforded **21** as an amorphous powder (from H_2O–MeOH), mp 235–238° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1740, 1700, 1690 (ester). ^{13}C NMR: δ52.2 (*q*, COOMe), 103.9 (*d*, anomeric C), 105.1 (*d*, anomeric C × 2), 166.6 (*s*, RCOO–), 176.2 (*s*, RCOO–), 170.0 (*s*, COOMe).

PS-B (**4**). Colourless needles (from *n*-BuOH–MeOH–H_2O), mp 285–290° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1720, 1710 (ester), 1610 (COO^-). Compound **4** was homogeneous on TLC and HPLC (same conditions as for **3**) and gave **1** and **2** on enzymatic hydrolysis and a monomethyl ester (**22**) as in **3**. Compound **22**, amorphous powder from MeOH–H_2O, mp 212–216° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1740, 1690, 1680 (ester). ^{13}C NMR: δ52.4 (*q*, COOMe), 103.5, 104.1, 105.1, 108.6 (each *d*, anomeric C × 4), 166.6 (*s*, RCOO–), 176.3 (*s*, RCOO–), 170.3 (*s*, COOMe).

Alkaline hydrolysis of **3** *providing* **5**. Compound **3** (260 mg) was boiled with 4% (w/v) K_2CO_3 in 90% MeOH for 1.5 hr, the reaction mixture was neutralized with dil. HCl, diluted with H_2O and extracted with *n*-BuOH. The organic layer, showing one spot (R_f 0.42) on TLC (silica gel; solvent a), was evapd *in vacuo* and the residue was passed through a Sephadex LH-20 column (eluant MeOH) to give an amorphous powder (**5**) (from MeOH–H_2O) (130 mg), mp 276–278° (decomp.), $[\alpha]_D$ +2.5° (H_2O; *c* 0.8). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1605 (COO^-). Compound **5** was refluxed with 2 N H_2SO_4 in 50% EtOH for 2 hr and then diluted with H_2O. The ppt. was collected by filtration, dried and recrystallized from Me_2CO to give colourless needles, mp 280–282°. The aglycone was identified with an authentic sample of A_1-barrigenol (**6**), by mmp, TLC and IR. The filtrate was neutralized with $Ba(OH)_2$ soln, filtered and the filtrate was concd and examined by TLC (Avicel; solvents d and e), and glucose, galactose and glr were detected. Methylation of **5** with CH_2N_2 in MeOH afforded **7** as colourless needles (from MeOH–EtOAc–H_2O), mp 278–282° (decomp.). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400 (OH), 1740 (ester). ^{1}H NMR (C_5D_5N): δ3.72 (3H, *s*, COOMe). ^{13}C NMR: δ52.1 (*q*, COO$\underline{\text{Me}}$), 103.8 (*d*, anomeric C), 105.0 (*d*, anomeric C × 2), 169.9 (*s*, $\underline{\text{C}}$OOMe). (Found: C, 55.65; H, 8.02. $C_{49}H_{80}O_{21}\cdot 3H_2O$ requires: C, 55.56; H, 8.18%.)

Methylation of **5** *by the Hakomori method*. Compound **5** (80 mg) was treated with NaH (300 mg) and MeI (3 ml) in DMSO (15 ml). The reaction mixture was diluted with H_2O, extracted with $CHCl_3$ and the $CHCl_3$ layer was washed, dried and evapd. The residue was chromatographed on silica gel (eluant *n*-hexane–EtOAc, 1:1) to give **8**, 40 mg, as an amorphous powder. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1750 (ester), no OH. FDMS *m/z*: 1186 $[M]^+$. ^{1}H NMR: δ4.50, 4.76, 4.84 (each 1H, *d*, $J = 6$, 8 and 8 Hz, anomeric H × 3).

Methanolysis of **8**. Compound **8** was heated with 7% HCl in MeOH for 2 hr, the mixture was treated with Ag_2CO_3 and filtered. The filtrate was evapd and the residue (methanolysate) was examined by TLC (silica gel; solvent b) and GLC (condition a), and one aglycone (**9**) and three methylated sugars were detected. Two of the sugars were identified as S-1 and S-2 by comparison with the authentic samples. The methanolysate was chromatographed on silica gel (eluant C_6H_6–Me_2CO, 80:1) to give **9**. Compound **9** was acetylated with Ac_2O–pyridine to give an acetate (**10**) as colourless needles (from Me_2CO–MeOH), mp 209–210°. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1730 (OAc), no OH. EIMS *m/z*: 588 $[M]^+$, 338. ^{1}H NMR: δ2.04 (3H, *s*, OAc), 3.27, 3.31, 3.35, 3.42 (each *s*, 3H, OMe × 4), 4.49 (1H, *t*-like, H-3).

Preparation of **11**. $NaBH_4$ (80 mg) was added to the soln of **8** (30 mg) in MeOH (7 ml) under ice-cooling and the reaction mixture was stirred for 20 hr at room temp. Me_2CO (2 ml) and H_2O (2 ml) were added to the mixture and evapd *in vacuo*, and the residue was diluted with excess H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was washed, dried and concentrated. The crude product was passed through silica gel CC (eluant $CHCl_3$–MeOH, 50:1) and the eluate was methylated by the Hakomori method to yield **11** (21 mg) as an amorphous powder. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: no ester and OH. FDMS *m/z*: 1172 $[M]^+$. ^{1}H NMR: δ4.29, 4.88, 4.96 (each 1H, *d*, $J = 6$, 8 and 8 Hz, anomeric H × 3).

Methanolysis of **11**. Compound **11** was methanolysed and worked up in the same manner as for **8**. The methanolysate was examined by TLC (silica gel; solvent b) and GLC (condition b), and **9**, S-1, S-2 and the methyl pyranoside of 4,6-di-*O*-methyl-glucose were detected.

Preparation and methanolysis of **12**. Compound **11** was heated with 0.7% HCl in MeOH for 2 hr and worked up as for **8**. The mixture showing three spots (R_f 0.22 (**11**), 0.32, 0.80) on TLC (silica gel; solvent *n*-hexane–EtOAc, 1:2) was chromatographed on silica gel (eluant *n*-hexane–EtOAc, 2:3) to give a compound (R_f 0.32), and the compound was methylated by the Hakomori method to yield **12** as an amorphous powder. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: no OH. ^{1}H NMR: δ4.29, 4.67 (each 1H, *d*, $J = 7$ and 7 Hz, anomeric H × 2). Compound **12** was subjected to methanolysis as for **8**, and **9**, S-1 and methyl 3,4,6-tri-*O*-methyl-glucopyranoside were obtained (TLC silica gel; solvent b, GLC condition a).

Alkaline hydrolysis of **4** *yielding* **13**. Compound **4** (570 mg) was hydrolysed with alkali and worked up in the same manner as for **3** to provide **13** (300 mg) as an amorphous powder (from MeOH–H_2O) (R_f 0.36, silica gel; solvent a), mp > 300° (decomp.), $[\alpha]_D$ −5.9° (MeOH; *c* 0.7). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400 (OH), 1600 (COO^-). On hydrolysis with acid under the same conditions as for **5**, compound **13** gave **6** and a sugar mixture. The sugar mixture was found to consist of arabinose, glucose and glr (TLC: Avicel; solvent d and e) and was chromatographed first over silica gel (eluant $CHCl_3$–MeOH–H_2O, 7:3:0.5) and then over Sephadex LH-20 (eluant MeOH) to give two kinds of sugars: a colourless syrup, $[\alpha]_D$ +82.0° (24 hr) (H_2O; *c* 1.5) (L-arabinose); a colourless syrup, $[\alpha]_D$ +53.2° (22 hr) (H_2O; *c* 0.9) (D-glucose). Monomethyl ester **14** of **13** (CH_2N_2), colourless needles (from MeOH–EtOAc–H_2O), mp 248–252° (decomp.), $[\alpha]_D$ −21.2° (MeOH; *c* 0.9). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400 (OH), 1740 (ester). ^{1}H NMR (C_5D_5N): δ3.76 (3H, *s*, COOMe). ^{13}C NMR: δ52.4 (*q*, COO$\underline{\text{Me}}$), 103.5, 104.0, 105.2, 108.7 (each *d*, anomeric C × 4), 170.3 (*s*, $\underline{\text{C}}$OOMe). (Found: C, 53.74; H, 7.80. $C_{53}H_{86}O_{24}\cdot 4H_2O$ requires: C, 53.98; H, 8.03%.)

Permethylate **15** *of* **13** (*Hakomori method*). Conducted in the same manner as for **5** to give **15** as an amorphous powder. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1740 (ester), no OH. FDMS *m/z*: 1302 $[M]^+$. ^{1}H NMR: δ4.43, 4.85, 4.98 (each 1H, *d*, $J = 6$, 6 and 8 Hz, anomeric H × 3), 5.08 (1H, *s*, anomeric H of arabinofuranose). Methanolysis of **15** in the same way as for **8** afforded **9** and four kinds of methylated sugars. Three of the sugars were identified as S-1, S-3 and S-4 by comparison with authentic specimens (TLC: silica gel; solvent b; GLC: condition a).

Synthesis and methanolysis of **16**. Reduction followed by methylation of **15** in the same manner as for **11** afforded **16**. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: no ester and OH. FDMS *m/z*: 1288 $[M]^+$. ^{1}H NMR: δ4.26, 4.92, 5.06, 5.20 (each 1H, anomeric H × 4). Methylated monosaccharides obtained by methanolysis of **16** were identified as S-1, S-3, S-4 and the methyl pyranoside of 6-*O*-methyl-glucose (TLC: silica gel; solvent b and $CHCl_3$–MeOH–H_2O, 7:3:0.3; GLC: condition a).

Partial hydrolysis of **13** *with a crude hesperidinase*. Compound **13** in 0.2 M KH_2PO_4 was incubated with a crude hesperidinase at 37° for 1 day, and the product was extracted with *n*-BuOH. The extracts showing the major spots [R_f 0.57 and 0.36 (**13**)] in TLC (silica gel: solvent a) were evapd and chromatographed on silica gel (eluant $CHCl_3$–MeOH–HOAc–H_2O, 12:4:1:1) to give **17** (R_f 0.57) as an amorphous powder (from MeOH–EtOH–EtOAc–H_2O), mp 276–280° (decomp.), $[\alpha]_D$ −16° (MeOH; *c* 0.8). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3395 (OH), 1605 (COO^-). Compound **17** gave **6**, arabinose and glr on acid hydrolysis as before.

Preparation of **18** *and its methanolysis*. Compound **17** was methylated by the Hakomori method to give its permethylate. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1750 (ester), no OH. ^{1}H NMR: δ4.31, 4.66 (each 1H, *d*, $J = 8$ and 6 Hz, anomeric H × 2), 5.02 (1H, *s*, anomeric H). The permethylate was reduced, followed by methylation, as usual to give **18**. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: no OH. FDMS *m/z*: 1084 $[M]^+$. ^{1}H NMR: δ4.25, 4.71 (each 1H, *d*, $J = 7$ and 7 Hz, anomeric H × 2), 5.22 (1H, *s*, anomeric H of arabinofuranose). Compound **18** was subjected to methanolysis, and the methanolysate was examined by TLC (silica gel; solvent b) and GLC (conditions a and b), and S-3, S-4 and the methyl pyranoside of 2,6-di-*O*-methyl-glucose were detected.

Mild acid hydrolysis of **13** *giving* **19**. Compound **13** was heated with 0.1 N H_2SO_4 in 50% EtOH for 16 hr at 70°. The mixture was neutralized with K_2CO_3, diluted with H_2O and extracted with *n*-BuOH. The BuOH layer showing a major spot (R_f 0.44) on TLC (silica gel; solvent a) was concd and the residue was subjected to silica gel CC (eluant $CHCl_3$–MeOH–HOAc–H_2O, 15:9:1:2), and the major product **19** was obtained. Amorphous powder (from MeOH–EtOH–H_2O), mp > 284° (decomp.), $[\alpha]_D$ +7.6° (H_2O; *c* 0.7). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400 (OH), 1605 (COO^-). Acid hydrolysis of **19** with 2 N H_2SO_4 in 50% EtOH afforded **6**, arabinose, glucose and glr.

Synthesis of **20** *and its methanolysis*. In the same manner as for

18, compound **20** was prepared from **19**. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no ester and OH. FDMS *m/z*: 1128 $[M]^+$. ^{1}H NMR: δ4.28, 4.89, 4.90 (each 1H, *d*, $J = 6$, 6 and 8 Hz, anomeric H × 3). Compound **20** was methanolysed as before to give **9**, S-1, S-3 and methyl 4,6-di-*O*-methyl-glucopyranoside.

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